



Short communication

Ni/La₂O₃ catalyst containing low content platinum–rhodium for the dehydrogenation of N₂H₄·H₂O at room temperature



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H I G H L I G H T S

- Novel Ni_{0.90}Pt_{0.05}Rh_{0.05}/La₂O₃ nanoparticles were prepared by a facile coreduction method.
- The catalyst exhibits high activity and 100% H₂ selectivity for the dehydrogenation of N₂H₄·H₂O.
- The obtained promising results will prompt the practical application of N₂H₄·H₂O.

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Ni/La₂O₃ nanocatalyst with Pt and Rh content as low as 5 mol%, respectively, is successfully synthesized by a facile co-reduction method in the presence of hexadecyl trimethyl ammonium chloride aqueous solution under ambient atmosphere. Interestingly, the resulted Ni/La₂O₃ catalyst with low cost exhibits excellent catalytic activity to dehydrogenation of hydrous hydrazine (N₂H₄·H₂O), producing hydrogen with 100% selectivity at room temperature (298 K), which represents a promising step toward the practical application for N₂H₄·H₂O system on fuel cells.

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1. Introduction

Hydrogen (H₂) is one of the sustainable and environmentally attractive energy carriers, and the controlled storage is a great challenge in the fuel cell-based H₂ economy [1–4]. Typical methods for H₂ storage, such as high-pressure gas containers, cryogenic liquid/gas containers, metal/complex hydrides, carbon materials, and metal-organic frameworks are suffering from obstacles in safety and efficiency [1,5,6]. Consequently, H₂ stored in some stable chemical compounds is desired [7,8].

Recently, hydrazine monohydrate (N₂H₄·H₂O), which is a liquid in a wide range of temperature (213–392 K) and contains high H₂ content (8.0 wt%), has attracted a great of research interests for promising H₂ production technology applications due to the reaction of N₂H₄ → N₂ + 2H₂ [9–26]. However, the key to use

effectively its H₂ storage potential is to avoid its undesired incomplete decomposition: 3N₂H₄ → 4NH₃ + N₂ [15–18]. The reaction pathway strongly depends on the catalysts and the reaction conditions [19–29].

Recent studies have shown that 100% H₂ selectivity for the dehydrogenation of N₂H₄·H₂O can be achieved by using Ni-based bimetallic catalysts. Nevertheless, their catalytic activities for this reaction at 298 K are still very low [22–28]. Moreover, most of the reported catalysts are noble metal or high noble metal loading [22–24,26–28], hindering their large scale applications because of the high costs and scarcities. Therefore, great effort has been made to solve the above problem, and some of non-noble-metal catalysts, such as Ni–Fe [25], Ni–Al₂O₃–HT [29], and NiMoB–La(OH)₃ [40], are found to have the certain catalytic activities for dehydrogenation of N₂H₄·H₂O. However, most of these reported catalysts were inactive at 298 K [25,29,40]. Thus, the development of a low noble metal loading catalyst with high catalytic activity and 100% H₂ selectivity for the dehydrogenation of N₂H₄·H₂O at 298 K is a desired goal.

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Herein, we prepare a low noble metal loading $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ catalyst by a facile surfactant-aided co-reduction method and investigate its catalytic performance toward the dehydrogenation of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. Unexpectedly, the $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ catalyst exhibits high catalytic activity and 100% H_2 selectivity for H_2 generation from $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ at 298 K. This excellent catalytic performance should be understood as the combinative effect of Ni, Pt, and Rh elements and also the cooperative effect of $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}$ nanoparticles (NPs) with La_2O_3 . Such synergistic effects among these counterparts not only reduce the use of noble metals, but also enhance the catalytic performance for the dehydrogenation of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ at 298 K.

2. Experimental details

2.1. Chemicals

$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd, 85%), nickel (II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd, >98%), Potassium hexachloroplatinate (IV) (K_2PtCl_6 , Sinopharm Chemical Reagent Co., Ltd, Pt 40.0–40.3%), Rhodium trichloride hydrate ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, Aladdin chemistry Co., Ltd, Rh 38.5–42.5%), Lanthanum (III) nitrate hydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd, >98%), sodium borohydride (NaBH_4 , Sinopharm Chemical Reagent Co., Ltd, >96%), sodium hydroxide (NaOH, Beijing Chemical Works, 96%), and hexadecyl trimethyl ammonium chloride (CTAC, Aladdin chemistry Co., Ltd, >99%) were used without further purification. De-ionized water with the specific resistance of 18.2 M Ω cm was obtained by reversed osmosis followed by ion-exchange and filtration.

2.2. Synthesis of catalysts

Catalysts of $\text{NiPtRh}/\text{La}_2\text{O}_3$ were synthesized through a surfactant-aided co-reduction method under ambient atmosphere at 298 K. Typically, for preparation of $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ (20 mol% of La_2O_3), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (53.5 mg), K_2PtCl_6 (6.0 mg), $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (2.6 mg), and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (16.2 mg) were dissolved along with CTAC (80.0 mg) in 4.0 mL water followed by ultrasonication for 5 min. 40.0 mg of NaBH_4 was dissolved in 1.5 mL water and then rapidly added into the above solution with magnetic stirring. After a few minute, a black suspension of NPs was obtained.

$\text{NiPtRh}/\text{La}_2\text{O}_3$ catalysts (20 mol% of La_2O_3) with different molar ratios of Ni:Pt:Rh were also synthesized by the above method in CTAC. When the molar ratio of Ni:(Pt + Rh) was kept as 0.9, the molar ratio of Rh:(Pt + Rh) (x value in $\text{Ni}_{0.90}(\text{Pt}_{1-x}\text{Rh}_x)_{0.10}/\text{La}_2\text{O}_3$) was changed from 0 to 1.0 (0, 0.3, 0.5, 0.7, 1.0). When the molar ratio of Rh:Pt was kept as a constant of 1.0, the molar ratio of (Pt + Rh):Ni (y value in $\text{Ni}_{1-y}(\text{Pt}_{0.5}\text{Rh}_{0.5})_y/\text{La}_2\text{O}_3$) was changed with several values (0 mol%, 2.5 mol%, 5.0 mol%, 7.5 mol%, 10.0 mol%, 20.0 mol%, 30.0 mol%, 40.0 mol%).

The $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ catalysts with other molar contents of La_2O_3 (0 mol%, 14 mol%, 20 mol%, 26 mol%) were also prepared in CTAC as the same method by changing the addition content of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

2.3. Characterizations

Powder X-ray diffraction (XRD) patterns were performed on a Rigaku RINT-2000 X-ray diffractometer with Cu K α . Transmission electron microscope (TEM, Tecnai F20, Philips) and corresponding energy-dispersive X-ray (EDX) spectrometry were applied for the detailed microstructure and composition analyses. X-ray photoelectron spectrometry (XPS) was acquired with an ESCALABMK II

(Vacuum Generators) spectrometer using Al K α X-rays (240 W). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurement was performed on a Thermo Jarrell Ash (TJA) Atomscan Advantage instrument. Mass spectrometry (MS) analysis for the generated gas was performed on an OmniStar GSD320 mass spectrometer, wherein Ar is chosen as the carrying gas.

2.4. Catalytic activity

Typically, the as-prepared $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ (20 mol% of La_2O_3) catalyst (0.25 mmol dissolved in 5.5 mL water) was kept in a two-necked round bottom. One neck of the flask was connected to a gas burette, and the other was connected to a pressure-equalization funnel to introduce 5.0 mL aqueous solution containing $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (0.5 M) and NaOH (0.5 M). The catalytic reaction was initiated once the aqueous solution of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and NaOH was introduced into the reaction flask containing the catalyst with magnetic stirring. The released gas was identified by MS, and its amount was volumetrically monitored using the gas burette at 298 K under ambient atmosphere.

The catalytic activities of other catalysts for this reaction were also applied as the above method. The molar ratios of metal: $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ for all the catalytic reaction were kept as a constant of 0.1.

3. Results and discussion

3.1. Characterizations

Fig. 1a shows the typical TEM image of the as-prepared $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ (20 mol% of La_2O_3). It can be seen that the NPs are well-dispersed with an average particle size of 2.0 nm (Fig. 1c). Fig. 1b is a high-resolution TEM (HRTEM) image of a single particle. The lattice fringes are measured to be 0.212 nm, which is similar to that of the (111) plane of face-centered cubic (fcc) Ni (JCPDS: 04-0850) [30]. The selected-area electron diffraction (SAED) pattern (Fig. 1b, insert) also reveals the crystalline nature of the NPs. The corresponding EDX spectrum displays all the existences of Ni, Pt, Rh, and La elements (Fig. S1). The Ni/Pt/Rh atomic ratio of the $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}$ catalyst has been confirmed by ICP-AES measurements (87.3:4.2:8.5 Ni/Pt/Rh).

In contrast, without addition of La precursors, the resulted $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}$ NPs have a larger average particle size of 3.2 nm than those prepared with La precursors (Fig. 1d and f). However, the HRTEM (Fig. 1e) and SAED (Fig. 1e, inset) of $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}$ show the similar crystal structure with that of $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$. Therefore, it suggests that the addition of $\text{La}(\text{NO}_3)_3$ during the synthetic process can effectively reduce the sizes of the NPs, leading to the more active sites of metal in the surfaces of NPs [31].

XRD pattern for the $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ NPs is compared with that of NPs prepared by the similar method only with La precursors (Fig. 2, black trace). According to the XRD results, it can be seen clearly that $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ NPs are composed of La_2O_3 [32,33] and alloy of Rh, Pt, and Ni.

Additionally, XPS is applied to analyze the chemical states of metal elements in the as-prepared sample, which revealed that the nanocatalyst is composed of Pt^0 , Rh^0 , Ni^0 and La_2O_3 [22,35–37,41]. The observed Rh 3d $_{5/2}$ and Rh 3d $_{3/2}$ binding energies (Fig. S2a) at 307.2 and 311.5 eV correspond to Rh^0 [22], and the Pt 4f $_{7/2}$ and Pt 4f $_{5/2}$ binding energies (Fig. S2b) at 70.6 and 73.8 eV also correspond to Pt^0 [41]. It is known that the La 3d $_{3/2}$ peak overlap Ni 2p $_{3/2}$ peak, the complex structures of the La 3d $_{3/2}$ spectra complicate Ni 2p $_{3/2}$ profile analyses. As shown in Fig. 3, Ni 2p $_{3/2}$ core level spectra cannot be analyzed separately without La 3d $_{3/2}$ core level spectra analysis [37], but Ni 2p $_{1/2}$ binding energy at 874.4 eV correspond to

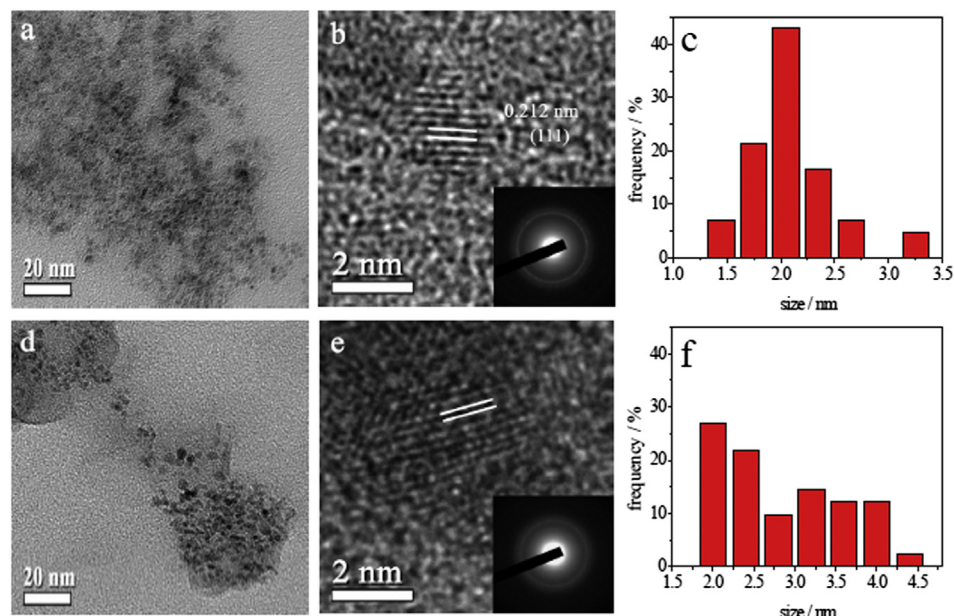


Fig. 1. (a, d) TEM images, (b, e) HRTEM images and its corresponding SAED patterns (inset), (c, f) particle size distribution for the Ni_{0.90}Pt_{0.05}Rh_{0.05} NPs prepared with and without La₂O₃ (20 mol%).

Ni⁰ [22]. La 3d_{5/2} peak and its satellite peak are noticeably dependent on the local chemical environment of La³⁺ ions [34–38]. The satellite peak of the La 3d_{5/2} core level in insulating compounds on the higher binding energy side is separated from the main peak by about 4 eV. Namely, the energy splitting is 4.2 and 3.3 eV for oxide and hydroxide species, respectively [37], while the energy splitting for highly dispersed La₂O₃/Al₂O₃ system is as low as 3.7–3.8 eV [38]. As shown in Fig. 3, the energy splitting of the La 3d_{5/2} in the as-prepared sample is 4.0 eV, suggesting La is in the oxidized state of La₂O₃ [35,36].

3.2. Catalytic activity

The catalytic activities of the as-prepared NiPtRh/La₂O₃ catalysts with different composition have been investigated toward the dehydrogenation of N₂H₄·H₂O at 298 K. It is found that the catalytic

activity and H₂ selectivity of the as-prepared catalyst strongly depend on the composition of Ni, Rh, Pt, and La₂O₃. As can be seen from Fig. 4a, the Ni_{0.90}Pt_{0.05}Rh_{0.05}/La₂O₃ catalyst exhibits the highest activity (18 min) and 100% H₂ selectivity. The initial TOF value calculated [Eq. (S1)] [42] over the catalyst is 45.9 h^{−1}, which is superior to the reported Ni–Pt [23,27,42] and Rh–Ni alloy catalysts [19,22,26] (Table S1). In Fig. 4a, higher or lower content of Rh in the Ni_{0.90}(Pt_{1−x}Rh_x)_{0.10}/La₂O₃ system result in much lower activity. In addition, the effects of the molar ratio (y) of Ni and (Pt + Rh) in Ni_{1−y}(Pt_{0.5}Rh_{0.5})_y/La₂O₃ system have also been investigated. As shown in Fig. 4b, the NiPtRh/La₂O₃ catalysts with (Pt + Rh) contents in the range of 7.5–30.0 mol% exhibit 100% H₂ selectivity at 298 K. Considering the high cost of the noble metal Pt and Rh and the obtained catalytic performance of the catalyst, the best Ni:(Pt + Rh) is fixed to be 9:1 (y = 0.1).

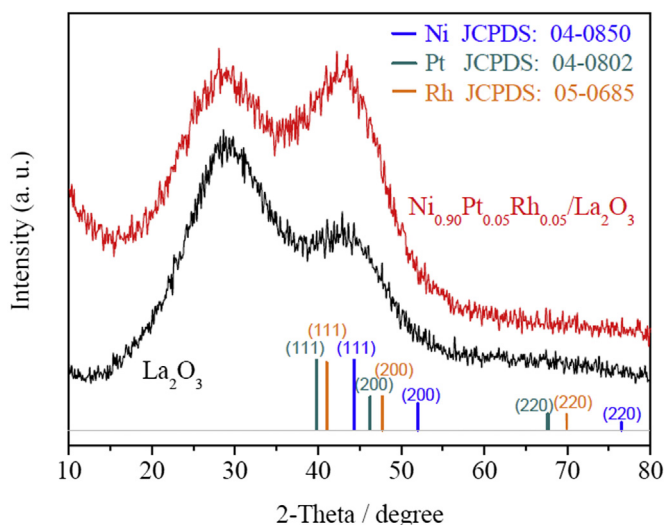


Fig. 2. X-ray diffraction patterns for Ni_{0.90}Pt_{0.05}Rh_{0.05}/La₂O₃ catalyst and pure La₂O₃.

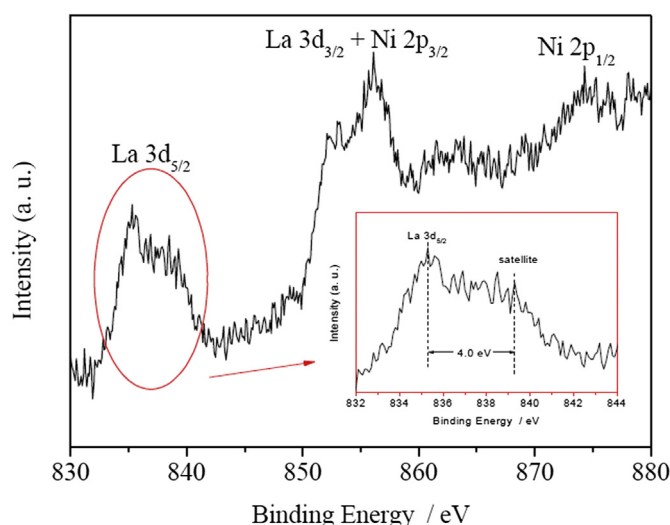


Fig. 3. XPS spectra of La 3d and Ni 2p for the Ni_{0.90}Pt_{0.05}Rh_{0.05}/La₂O₃ catalyst.

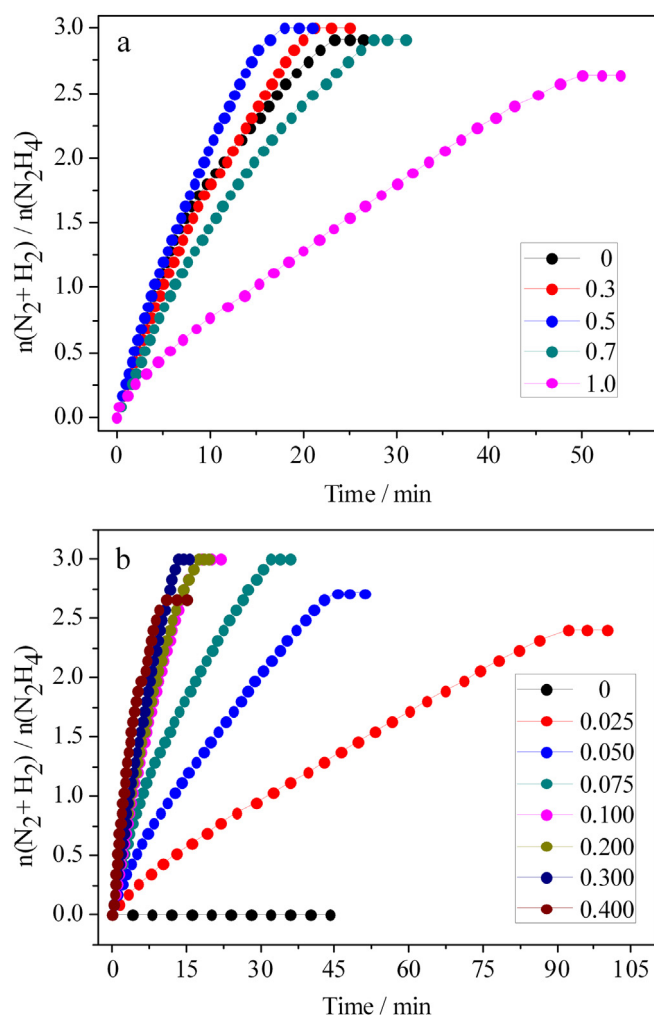


Fig. 4. Time course plots for the dehydrogenation of 5 mL aqueous solution of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (0.5 M) and NaOH (0.5 M) catalyzed by (a) $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ ($x = 0-1.0$) and (b) $\text{Ni}_{1-y}(\text{Pt}_{0.5}\text{Rh}_{0.5})_y/\text{La}_2\text{O}_3$ ($y = 0-0.4$) at 298 K (metal/ $\text{N}_2\text{H}_4 = 1:10$).

On the other hand, to investigate the dependence of the catalytic activity and H_2 selectivity on the La_2O_3 ratio, the catalysts prepared without or with different amount of La precursors were examined (Fig. 5). It is found that the activity and H_2 selectivity of the catalysts for this reaction increase with the increasing content of La_2O_3 up to 20 mol%. However, further increase in La_2O_3 content results in lower catalytic activity and H_2 selectivity. For example, only 3.0 equiv of gases can be released within 18 min with $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ catalyst (20 mol% of La_2O_3).

The generated gas over $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ catalyst is identified by MS to be H_2 and N_2 , indicating the complete decomposition of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ into H_2 and N_2 at 298 K (Fig. S3). It is noteworthy that pure La_2O_3 exhibits no activity towards the dehydrogenation of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ under similar conditions (Fig. S4). The above results suggest that La_2O_3 plays a critical role in improving the catalytic performance of $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}$, which might be attributed to the strong basic site of additional effects of La_2O_3 [39]. As for the catalytic decomposition of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, the selectivity of H_2 can be explained by facilitating the dissociation of N–H bond over catalyst [29], wherein the strong basic site is known to favor the selective cleavage of the N–H bond [29,40]. Therefore, the synergistic effect of $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}$ and strong basic sites of La_2O_3 can be reasonably responsible for the high H_2 selectivity and catalytic activity for dehydrogenation of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

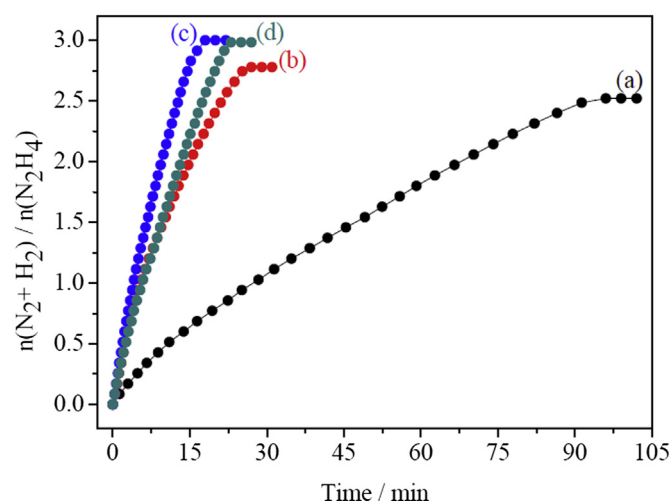


Fig. 5. Time course plots for the dehydrogenation of 5 mL aqueous solution of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (0.5 M) and NaOH (0.5 M) catalyzed by $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}$ in the presence of (a) 0 mol%, (b) 14 mol%, (c) 20 mol%, (d) 26 mol% La_2O_3 at 298 K (metal/ $\text{N}_2\text{H}_4 = 1:10$).

4. Conclusion

In summary, a facile co-reduction route is employed to synthesize novel $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}/\text{La}_2\text{O}_3$ NPs at 298 K under ambient atmosphere. When first used as heterogeneous catalyst for dehydrogenation of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, superior catalytic performances including high activity and 100% H_2 selectivity are successfully obtained even at 298 K, which might be due to the synergistic effect of unique composition of Ni, Pt, and Rh in $\text{Ni}_{0.90}\text{Pt}_{0.05}\text{Rh}_{0.05}$ and strong basic sites derived from the incorporation of the La_2O_3 . The obtained promising results open new excited possibility for the development of next generation cost-effective and highly efficient dehydrogenation catalysts to meet the requirement of practical application of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.03.059>.

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